Bonding, Structure, and Magnetism of Physisorbed and Chemisorbed O_2 on Pt(111)

W. Wurth,[1] J. Stöhr,[2] P. Feulner,[1] X. Pan,[2] K. R. Bauchspiess,[2] Y. Baba,[1] E. Hudel,[1] G. Rocker,[1] and D. Menzel[1]

[1]*Institut für Festkörperphysik E20, Technische Universität München, D-8046 Garching, Germany*
[2]*IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099*
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Near-edge x-ray-absorption fine-structure spectroscopy studies are used to determine changes in the electronic, geometric, and magnetic structure of two sequential molecular precursors of O_2 on Pt(111). Both molecules lie down on the surface. Physisorbed O_2 is found to be van der Waals bonded, structurally unperturbed, and paramagnetic, while chemisorbed O_2 is π bonded, stretched by 0.16 Å, and exhibits a reduced or vanishing paramagnetic exchange splitting.

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Trapping into a physisorbed state, chemisorption and dissociation are believed to be fundamental steps in gas-surface interactions and, in some cases, such a sequence of events has indeed been verified by experiment.[1-3] Despite the proven existence of physisorbed (van der Waals bonded) and chemisorbed (chemically bonded) molecular precursors to dissociation there are many unanswered questions regarding the electronic, geometric, and magnetic structure of molecules in such states. The present study was undertaken to shed light on this problem and it provides definitive answers with respect to the nature of the molecule-substrate bond, the molecular orientation, the intramolecular bond length, and the magnetic properties of O_2 adsorbed on Pt(111) in two different states.

The O_2/Pt(111) system was chosen because two well defined sequential molecular precursors have been previously identified for this system.[4] Under controlled experimental conditions the physisorbed state ($T < 30$ K) can be converted by heating into the chemisorbed state, allowing a direct characterization of the two states. Also, the open-shell oxygen molecule is particularly interesting in that it is paramagnetic in its $^3\Sigma$ ground state and might therefore exhibit changes in its magnetic properties arising from molecule-substrate interactions. Indeed, we unambiguously establish a change in the magnetic structure of the molecule between the physisorbed and chemisorbed states, as revealed by a pronounced reduction in the exchange splitting of the σ^* resonance for chemisorbed relative to physisorbed O_2. Our identification of such an exchange splitting in the K-shell excitation spectra of the oxygen molecule is new and supported by self-consistent-field $X\alpha$ multiple-scattering calculations. We also find that in the low-temperature physisorbed state the intramolecular structure of O_2 is nearly indistinguishable from that of van der Waals bonded solid O_2 and we therefore attribute its bond to the surface to a van der Waals interaction. O_2 lies down in both the physisorbed as well as the higher-temperature chemisorbed state. In this latter state, the nature of the molecule-surface bond is directly revealed by the near-edge x-ray-absorption fine-structure (NEXAFS) spectra. The resonance associated with the π^* orbital perpendicular to the surface is weakened and broadened due to its involvement in the chemisorption bond, while the resonance corresponding to the π^* orbital parallel to the surface remains unperturbed. A $\simeq$5-eV shift of the σ^* resonance indicates a 0.16-Å bond lengthening in the chemisorbed phase relative to the physisorbed phase which is found to have the same bond length as free O_2 (1.21 Å).

Experiments were carried out at the storage ring BESSY in Berlin, using the SX700-I monochromator. At the oxygen K edge the monochromator energy resolution was about 0.6 eV during the present experiments. The monochromator energy was calibrated to ± 0.3 eV by photoemission spectra of the Pt $4f$ peaks, taken in the range 500 eV $\leq h\nu \leq$ 600 eV. NEXAFS spectra were recorded in the partial electron yield mode and normalization was accomplished by dividing the spectra for O_2/Pt(111) by those of the clean surface.[5] Spectra were taken at 7° glancing x-ray incidence (**E** vector 7° from surface normal) and normal incidence (**E** in surface plane). Oxygen multilayers and the physisorbed molecular state were prepared by controlled O_2 exposures of the clean Pt(111) crystal at 17 K. The temperature dependence of O_2 adsorption was characterized in detail by temperature programed desorption measurements. It was found that the conversion to chemisorbed O_2 starts around 30 K, and the chemisorbed state was prepared either by heating the physisorbed layer to 80 K or by dosing the Pt(111) crystal at 80 K. Both procedures led to nearly identical spectra. All measurements were made at 17 K.

Figure 1 shows a comparison of the polarization-dependent NEXAFS spectra for a thin multilayer ($\simeq$9 monolayers), and monolayers of physisorbed and chemisorbed O_2. The spectra strongly resemble that of gas-phase O_2 [see Fig. 2(d) below].[6] The resonances are assigned with the help of the results of a self-consistent spin-dependent $X\alpha$ multiple-scattering (MS) calculation shown in Fig. 2(c). The calculation utilized Slater's

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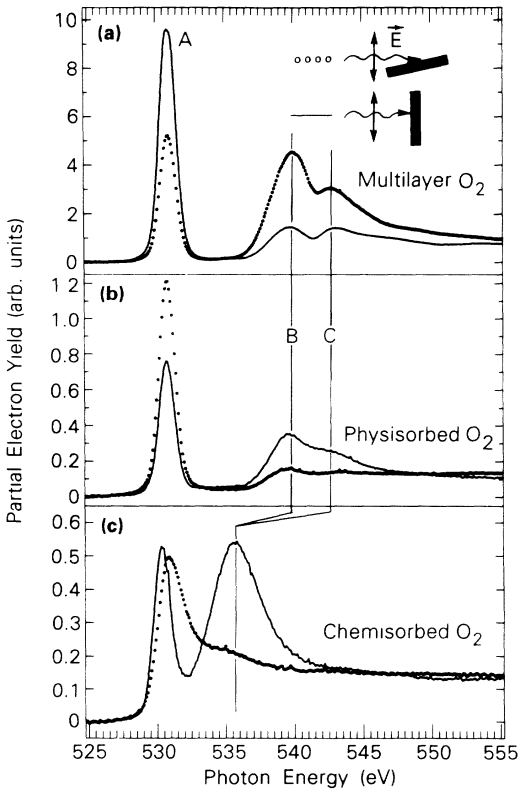

FIG. 1. Partial electron yield NEXAFS spectra of a thin O_2 multilayer condensed on Pt(111) and of physisorbed and chemisorbed O_2 on Pt(111). The spectra plotted as data points were recorded at 7° glancing x-ray incidence (**E** vector 7° from surface normal), those as solid lines at normal incidence (**E** vector in surface plane). All spectra are normalized to the incident flux and background.

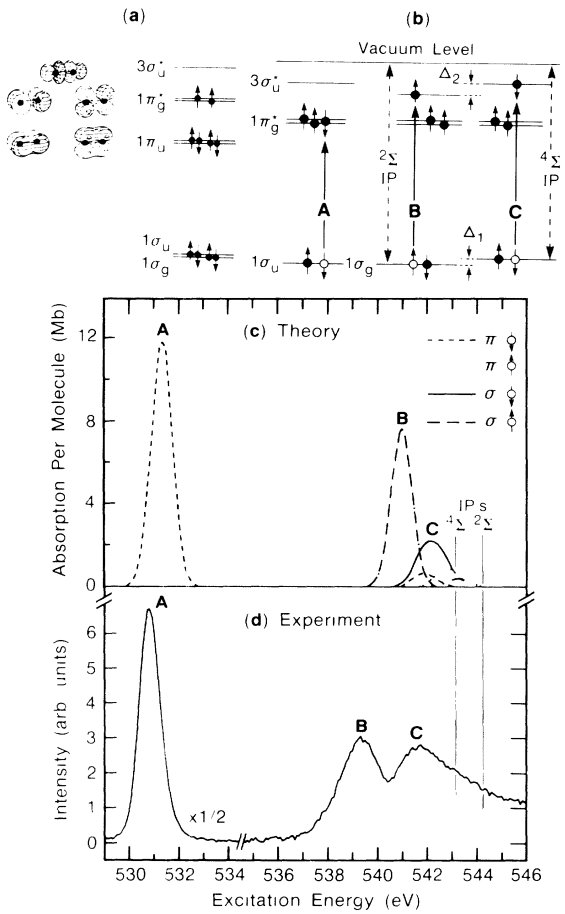

FIG. 2. (a) Orbital contour plots (Ref. 15) and schematic energy-level diagram for O_2 in its $^3\Sigma$ ground state. Note that the $1\sigma_u$ and $1\sigma_g$ orbitals, corresponding to the 1*s* shell, are degenerate. (b) Schematic energy-level diagram and transitions allowed by the dipole selection rule. The transitions labeled $^2\Sigma$ and $^4\Sigma$ correspond to the ionization potentials for excitation of a spin-up and spin-down electron from the 1*s* shell, respectively (Ref. 8). The exchange splitting in NEXAFS, $\Delta_2-\Delta_1$, arises from differences in the magnetic exchange interactions in the final states created by transitions *B* and *C* to the $3\sigma_u^*$ orbital. (c) Spin- and polarization-resolved NEXAFS spectrum calculated by means of self-consistent $X\alpha$ multiple-scattering theory. All calculated oscillator strengths were converted into cross sections by convolution with a Gaussian of 1.0 eV FWHM. The calculated ionization potentials (same as measured) corresponding to $^4\Sigma$ and $^2\Sigma$ ionic final states are also indicated. (d) Experimental electron-energy-loss spectrum of gas-phase O_2 (Ref. 12).

transition-state method and a semiempirical choice of the muffin-tin spheres,[7] i.e., adjustment of their radii to yield the spin-dependent experimental 1*s* ionization potentials[8] 543.1 eV ($^4\Sigma$ ionic final state) and 544.2 eV ($^2\Sigma$ ionic final state) for the O_2 molecule, as schematically indicated in the energy-level diagram shown in Fig. 2(b). Resonance *A* at $\simeq$531 eV is readily assigned as a $1\sigma_u \rightarrow 1\pi_g^*$ transition, and we shall refer to it as a π^* resonance. According to Hund's rule, in the ground state, the two degenerate $1\pi_g^*$ orbitals of O_2 are each singly occupied by electrons with parallel spins, and we shall assume that their spins are up as shown in Fig. 2(a). The Pauli principle and the dipole selection rule which forbids any spin-flip transition then demand that the π^* resonance corresponds to excitation of a spin-down electron from the 1*s* shell ($1\sigma_u$ orbital). Resonances *B* and *C* in Fig. 1 are assigned to σ^* resonances, and they correspond to spin-up and spin-down $1\sigma_g \rightarrow 3\sigma_u^*$ transitions, respectively, the splitting arising from two different final-state spin configurations, as shown in Fig. 2(b).

The measured exchange splitting of the σ^* resonance, given by $\Delta_2-\Delta_1$, is remarkably large ($\simeq$3 eV), and exceeds the calculated splitting (1.2 eV) shown in Fig. 2(c). This quantitative difference is due to the limited accuracy of the calculated transition energies[9] but it does not affect the qualitative reliability of the calculated spectra. Closer inspection of all transitions calculated by the $X\alpha$ MS method also reveals that the schematic molecular-orbital picture given in Fig. 2(b) is oversimplified in that it neglects the influence of Rydberg orbitals. The calculation predicts several transitions to

Rydberg orbitals which mostly fall in the region of resonance *C*. These transitions are also included in Fig. 2(c). In particular, resonance *C* itself is composed of two roughly equal components of spin-down character. We believe this splitting to arise from a mixing of Rydberg orbitals with the $3\sigma_u^*$ valence orbital. In NEXAFS spectra the valence component ($3\sigma_u^*$) dominates, in analogy to C-H*/Rydberg[10] and O-H*/Rydberg[11] resonances, and, in contrast to pure Rydberg resonances, such resonances remain largely unaffected by extramolecular bonds. This is supported by comparison of the gas-phase spectrum in Fig. 2(d)[12] with the spectra for solid O_2 and physisorbed O_2 on Pt(111) shown in Fig. 1. In the latter cases peak *C* has a reduced intensity owing to a quenching or broadening of the Rydberg components.[13] Therefore, the observed splitting between resonances *B* and *C* in Fig. 1 is attributed to a magnetic exchange-splitting effect.

The assignment of the symmetry character of the resonances allows us to unambiguously determine the molecular orientation. Since σ^* resonances have maximum intensity for **E** along the internuclear axis,[14] O_2 is oriented preferentially along the surface normal in the thin multilayer and it lies down on the surface in both the physisorbed and chemisorbed states. Curve fits assuming 85% linearly polarized x rays yielded tilt angles of the O-O axis from the surface plane of 55° for the multilayer and $<15°$ for the physisorbed and chemisorbed monolayers. For lying down O_2, any chemical bonding to the substrate has to involve the π system of the molecule. In fact, because there are two orthogonal π systems as illustrated by the orbital contour plots[15] for the bonding ($1\pi_u$) and antibonding ($1\pi_g^*$) π orbitals in Fig. 2(a), one would expect a difference between the π system parallel ($\pi_\parallel$) and perpendicular ($\pi_\perp$) to the surface. NEXAFS can distinguish between the two π^* orbitals because the π^* resonance corresponds to a $1\sigma \rightarrow \pi_\parallel^*$ transition for **E** parallel to the surface and $1\sigma \rightarrow \pi_\perp^*$ for **E** perpendicular to the surface. For physisorbed O_2, curve fitting of the π^* resonance gives the same width (1.37 eV FWHM) and position (530.7 eV) for both glancing- and normal-incidence spectra. These values are close to those found for the width (1.46 eV) and position (530.9 eV) of multilayer O_2. For chemisorbed O_2 the π^* resonance at normal incidence falls at 530.3 eV with a width of 1.37 eV while at glancing incidence it falls at 530.9 eV and is severely broadened with an asymmetric line shape.

These results indicate that for physisorbed O_2 there is no chemical bond to the surface via the π^* system, and the molecule-substrate interaction is of van der Waals nature, as in condensed O_2. In contrast, for chemisorbed O_2 the energetic inequivalence of the π^* resonances at normal and glancing incidence and the distortions of the π^* resonance at glancing incidence show a strong involvement of the $\pi_\perp^*$ orbital in the molecule-substrate bond. We attribute the broadening to a mixing of $\pi_\perp^*$-Pt

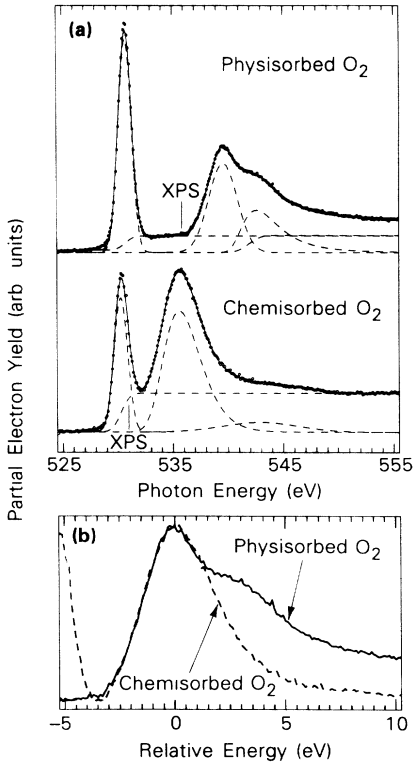

FIG. 3. (a) Curve-fitted normal-incidence NEXAFS spectra of physisorbed and chemisorbed O_2 on Pt(111), revealing the reduced exchange splitting and shift of the σ^* resonance for chemisorbed O_2. The XPS binding energy relative to the Fermi level is labeled XPS. (b) Comparison of σ^* resonances for physisorbed (solid) and chemisorbed (dashed) O_2, shifted in energy (relative shift 4.0 eV) and rescaled in amplitude to align the intensity maxima.

$d\pi$ orbitals with charge transfer from the metal into the $\pi_\perp^*$ orbital, rendering a superoxolike O_2^- species, as proposed before.[16] Note that for chemisorbed O_2 the $\pi_\parallel^*$ resonance (orbital) appears to be undistorted by the surface bond, as expected for a superoxolike species.

The structural differences of the two O_2 species is revealed most dramatically by the respective σ^* resonances, as shown in detail in Fig. 3. The exchange splitting, clearly seen in the spectrum of physisorbed O_2, is not evident for chemisorbed O_2. Curve fitting yields a splitting of 3.0 eV for the physisorbed species, as shown in Fig. 3(a). The low-energy peak at 539.6 eV is well fitted with a symmetric Gaussian (3.1 eV FWHM) while the high-energy peak at 542.6 eV has an asymmetric Gaussian profile, owing to the fact that it merges into the ionization continuum above the vacuum level with an onset of 541.9 eV.[17] For chemisorbed O_2 only a single pronounced σ^* resonance at 535.6 eV is observed and it can be accounted for by a single slightly asymmetric Gaussian. A weak broad feature at higher energy (543.0 eV) is attributed to scattering processes involving substrate atoms or to multielectron effects. The fit shown in Fig. 3(a) is the simplest possible way to account for the σ^*

resonance. We have also carried out fits with two Gaussians as for the spectrum of physisorbed O_2. From such fits we believe that an upper limit of the exchange splitting in chemisorbed O_2, if present at all, is 2.2 eV.

We attribute the reduction of the exchange splitting in chemisorbed O_2 to the strong interaction of the $\pi_\perp^*$ molecular orbital with the surface. Charge transfer from the substrate into this orbital will lead to a partial spin compensation, e.g., to a doublet ground state for an O_2^- species. This initial-state effect is expected to lead to a reduced exchange splitting in the final state. Another interesting possibility is a dynamical spin-relaxation effect. In NEXAFS an exchange splitting will only be observed if the spin-relaxation time of the electrons in the π^* orbitals is longer than the lifetime of the core excited final state. The relevant final-state lifetime can be estimated from the width of the σ^* resonance to be about 10^{-16} sec. Little is known about the spin-relaxation time of a paramagnetic molecule on a metal surface. From the failure of ESR experiments[18] to reveal any paramagnetic splitting for chemisorbed O_2 on Ag(110) and estimates based on spin-relaxation times of magnetic impurities in nonmagnetic hosts[19] it is believed that the spin-relaxation time of a paramagnetic molecule on a surface at 20 K is shorter than 10^{-12} sec. It is conceivable that while the spin-relaxation time for physisorbed O_2 is long compared to the final-state lifetime, it is comparable to it or even shorter than it for chemisorbed O_2 owing to the stronger coupling of the π electrons to the conduction-electron bath of the substrate. This would lead to a reduced or vanishing exchange splitting of the σ^* resonance.

For physisorbed O_2 the 539.6-eV position of the first σ^* resonance which is least affected by changes in overlapping Rydberg resonances is similar to the values 540.0 eV in multilayer O_2 and 539.3 eV for the gas phase. This indicates almost identical bond lengths (1.21 Å) in the three phases. Differences in intensity ratios and splittings between resonances *B* and *C* are largely attributed to changes in the Rydberg contribution of resonance *C*. We also note that solid O_2 is antiferromagnetic[20] which can affect the exchange splitting via the exchange interaction between adjacent oxygens. In contrast, Figs. 1 and 3 reveal a pronounced shift for chemisorbed O_2, $\simeq 5$ eV, using the centers of gravity of the respective σ^* resonances. This corresponds to a significant bond lengthening to 1.37 ± 0.05 Å for chemisorbed O_2.[21]

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[21]In our previous study (Ref. 16) we calibrated the energy in our NEXAFS spectra by aligning the onset of absorption with the measured x-ray photoemission spectroscopy (XPS) binding energy (530.8 eV). The present high-resolution measurements show that this procedure is incorrect because the π^* resonance actually falls at an energy less than the XPS binding energy. Hence the present value (1.37 ± 0.05 Å) for the bond length of chemisorbed O_2 is more reliable than the old value (1.32 ± 0.05 Å).